ADSORPTIONAL-KINETIC METHOD
OF DETERMINING BOND ENERGIES

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Before reacting, a molecule on a catalyst surface forms an adsorption, and then a catalytic complex. The characterization of such complexes makes it possible to look more deeply into the mechanism of the process and may throw light onto the nature of catalysis. Balandin [1] proposed a kinetic method of characterizing these complexes which made it possible to find the thermodynamic functions of adsorption complexes and determine the energies of bonds in the activated catalytic complex.

Below we propose a method for the determination of energies of the bonds of reacting atoms of the organic molecule with surface atoms of the catalyst which differs from the previously proposed kinetic method [2] in that it is here sufficient that the catalyst carry out only one reaction (in the kinetic method two or three are required, which is often not practicable) and in that this method, unlike the kinetic method, does not require the presupposition that several reactions are catalyzed by the same active center in the catalyst. All this permits a more profound characterization of the individuality of the active center.

The method is as follows. According to the multiplet theory, the activation energy for the dehydrogenation of an alcohol, for example, can be represented as the algebraic sum of energies of breaking and forming bonds in the activated complex.

\[ -\varepsilon = \sum \gamma_i Q_i, \]

in which \( Q \) is the energy required for the complete rupture of the bond \( i \), and the coefficient \( \gamma \) is the degree of deformation of the bond \( i \) and takes account of the fact that reaction starts very much earlier than the complete rupture of the bond. It was found [2] that \( \gamma \) can be taken outside the summation sign and that

\[ \gamma \approx 2/4. \]

For the dehydrogenation of an alcohol we may rewrite (1) as

\[ -\varepsilon = -\gamma Q_{C-H} - \gamma Q_{O-H} + 2\gamma Q_{H-K} + \gamma Q_{C-K} + \gamma Q_{O-K}. \]

It may be considered that for the heat of formation of the precatalysis adsorption complex an equation similar to (1) holds:

\[ \lambda = \sum \alpha_i Q_i. \]
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>α</th>
<th>Q_H–K</th>
<th>( \frac{Q_C–K}{Q_O–K} ) or ( \frac{Q_C–K + Q_O–K}{Q_H–K} )</th>
<th>ε</th>
<th>( \Delta \gamma_1 )</th>
<th>( \Delta \gamma_2 )</th>
<th>( \Delta \gamma_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0,759</td>
<td>55,0</td>
<td>86,1</td>
<td>8,9</td>
<td>3,7</td>
<td>14,5</td>
<td>—</td>
</tr>
<tr>
<td>Pt</td>
<td>0,611</td>
<td>46,5</td>
<td>93,6</td>
<td>17,2</td>
<td>0</td>
<td>-5,8</td>
<td>—</td>
</tr>
<tr>
<td>Co</td>
<td>0,690</td>
<td>50,4</td>
<td>92,7</td>
<td>12,4</td>
<td>0</td>
<td>0</td>
<td>—</td>
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<tr>
<td>Cu</td>
<td>0,667</td>
<td>50,6</td>
<td>93,6</td>
<td>10,1</td>
<td>0</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Cu*</td>
<td>0,659</td>
<td>50,1</td>
<td>36,8</td>
<td>55,4</td>
<td>12,8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag</td>
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<td>47,8</td>
<td>88,1</td>
<td>19,5</td>
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<td>0</td>
<td>—</td>
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<tr>
<td>Fe</td>
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<td>47,5</td>
<td>87,7</td>
<td>20,0</td>
<td>0</td>
<td>0</td>
<td>—</td>
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<tr>
<td>MnO</td>
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<td>27,8</td>
<td>39,9</td>
<td>31,8</td>
<td>-6,83</td>
<td>11,63</td>
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<tr>
<td>ZnO</td>
<td>0,741</td>
<td>50,6</td>
<td>93,0</td>
<td>11,4</td>
<td>8,5</td>
<td>8,1</td>
<td>—</td>
</tr>
</tbody>
</table>

The coefficients \( \gamma_1 \) and \( \alpha \) are different for a given \( Q \) because the positions of the atoms in the catalytic and adsorption complexes are energetically somewhat different. The difference between \( \gamma_1 \) and \( \alpha \) should not be great because the difference between the adsorption and catalytic complexes on a given active center be regarded as very slight.

We shall further consider that the reacting atoms of the organic molecule in the adsorption and catalytic complexes form bonds with surface atoms of the catalyst which are of approximately equal strength, i.e., we suppose that

\[
\gamma_{x–K} = \alpha_{x–K} \approx 0.75,
\]

but in order to preserve the distinction between adsorption and kinetic complexes we shall leave the coefficients \( \alpha \) in front of the energies of breaking bonds in organic molecules in the expression for the heat of adsorption and shall assume that they have some mean value \( \alpha \). For the heats of adsorption of the alcohol, aldehyde (or ketone), and hydrogen we then have, respectively:

\[
\begin{align*}
\lambda_1 &= -aQ_{C–H} - aQ_{O–H} + 2\gamma Q_{H–K} + \gamma Q_{C–K} + \gamma Q_{O–K}, \\
\lambda_2 &= -aQ_{C–O} + \gamma Q_{O–K} + \gamma Q_{C–K}, \\
\lambda_3 &= -aQ_{H–H} + 2\gamma Q_{H–K}.
\end{align*}
\]

Equations (2), (3), (6), (7), and (8) enable us to find the unknowns \( \alpha \) and \( Q_{x–K} \) if \( \lambda_1 \) has been determined. At present the methods of determination most developed give not individual \( \lambda_1 \), but the differences \( \lambda_1 - \lambda_A = \Delta \lambda_1 \), which are found in the study of the temperature dependence of the process of displacing the original substance by reaction products or extraneous matter from the active centers of the catalyst [1].

Subtracting (6) from (7) and (8), we find

\[
\Delta \lambda_21 = a (Q_{C–H} + Q_{O–H} - Q_{C–O}) - 2\gamma Q_{H–K}.
\]

Adding (3), (9), and (10), we obtain an equation for the calculation* of \( \alpha \):

\[
\Delta \lambda_{31} + \Delta \lambda_{32} - \varepsilon = a (2Q_{C–H} + 2Q_{O–H} - Q_{C–O} - Q_{H–H}) - \gamma (Q_{C–H} + Q_{O–H})
\]

*During the final editing of this paper we learned of the previous work of S. L. Kiperman, in which he analyzed analogous questions and came to somewhat different conclusions (this work will be published in the Zhurnal Fizicheski Khimii).